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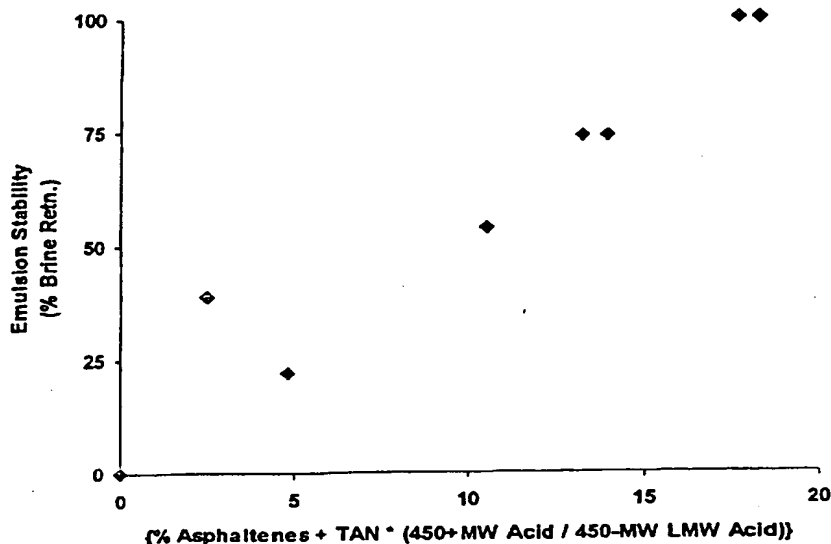
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(54) Title: IMPROVEMENTS IN OIL DESALTING BY FORMING UNSTABLE WATER-IN-OIL EMULSIONS

(57) Abstract: A method for determination for a given oil the relative stability of a water-in-oil emulsion that will be formed by that oil with water comprises measuring for the given oil the weight percent asphaltenes (A), total acid number (TAN), and ratio of the amount of naphthenic acids in the 450+ molecular weight to 450 molecular weight range (R); calculating an emulsion stability parameter, $S = A + TAN * R$; and determining whether the emulsion stability parameter, S, is greater than about 3; with a value above 3 being determinative of an emulsion more stable than one with a value less than 3.

IMPROVEMENTS IN OIL DESALTING BY
FORMING UNSTABLE WATER-IN-OIL EMULSIONS

FIELD OF THE INVENTION

[0001]   The invention relates generally to oil desalting and more particularly to improvements in the aqueous treatment of crude oils for desalting where water-in-oil emulsions are formed.

BACKGROUND OF THE INVENTION

[0002]   Removal of corrosive water-soluble salts, particularly chlorides of sodium and potassium from crude oil is an important processing operation in refining of crude oils. The process of desalting usually involves addition of 1 to 20 weight percent wash water to the crude oil, mixing to form a water-in-crude oil emulsion and then subjecting the water-in-crude oil emulsion to electrostatic demulsification or hydrocyclone treatment. Under the influence of electrostatic or centrifugal fields the dispersed water droplets coalesce and the water-in-oil emulsion is demulsified. Water and the water-soluble salts are separated from the crude oil and removed. Key to the efficiency of the desalting process is the formation of unstable water-in-oil emulsions. Most heavy crude oils that contain asphaltenes and naphthenic acids tend to form stable water-in-oil emulsions. These stable water-in-oil emulsions are difficult to demulsify and tend to form large volumes of a rag layer in the separator vessels. Rag layers are layers of water-in-oil emulsions and sub-micron size solids that form at the boundary between oil and water layers in separators. Formation of rag layers result in substantial oil loss and reduce the efficiency of dewatering and desalting processes. Current methods using centrifuges, hydrocyclones and electrostatic demulsifiers require large doses of demulsifier chemicals, high operation temperature and long residence times to desalt and/or dewater these water-in-oil

emulsions. Thus, there is a continuing need for improved cost effective methods to demulsify and desalt water-in-oil emulsions especially those formed from heavy crude oils. Further, there is a need to predict the ability of a heavy crude oil to form stable emulsions so that preventive measures can be undertaken prior to wash water addition and formation of water-in oil emulsions. The present invention addresses these needs.

SUMMARY OF THE INVENTION

[0003]   Broadly stated, the present invention provides a method to determine for a given oil the relative stability of an emulsion that will be formed by that oil with water and using that determination in desalting crude oils.

[0004]   The invention includes a method for determination for a given oil , especially crude oils, crude oil distillates, resids of crude oil distillation and mixtures thereof, the relative stability of a water-in-oil emulsion that will be formed by that oil with water comprising:

measuring for the given oil the weight percent asphaltenes (A), total acid number (TAN), and the ratio of the amount of naphthenic acids in the 450+ molecular weight to 450 molecular weight range (R);

calculating an emulsion stability parameter, $S = A + TAN * R$;

determining whether the emulsion stability parameter, S, is greater than about 3; with a value above 3 being determinative of an emulsion more stable than one with a value less than 3.

[0005]   The invention also includes an improved method to desalt a crude oil comprising:

measuring for the oil, the weight % asphaltenes (A),

total acid number (TAN),

the ratio of the amount of naphthenic acids in the 450+ molecular weight to 450 molecular weight range (R);

calculating an emulsion stability parameter, $S = A + TAN * R$,

determining whether the emulsion stability parameter, S , is greater than about 3, and, if above 3;

treating the oil under conditions sufficient to obtain a treated oil whose emulsion stability parameter S is less than about 3;

adding water to the said treated oil, in the range of 1 to 20 wt% based on the weight of the treated oil;

mixing the treated oil and water to form a water-in-treated oil emulsion;

coalescing the water of the water-in- treated oil emulsion;

separating the coalesced water to obtain a desalted crude oil.

BRIEF DESCRIPTION OF FIGURES

[0006]   Figure 1 is a plot of experimentally determined emulsion stability by berea filtration method versus S.

[0007]   Figure 2 is a plot of emulsion stability determined by berea filtration method versus electrostatic field method.

DETAILED DESCRIPTION OF THE INVENTION

[0008]   Hydrocarbon oils that contain asphaltenes and naphthenic acids such as crude oils tend to form water-in-oil emulsions with varying degrees of stability. The present invention is based on the discovery that the relative stability of a water-in-oil emulsions is related to an emulsion stability parameter (S) defined by the expression:

S = A + TAN * R wherein,

A is the weight in grams of asphaltenes present in 100 grams of the oil,

TAN is the total acid number of the oil, and

R is the ratio of the amount of naphthenic acids in the 450+ molecular weight to 450 molecular weight range.

[0009]   One significance of the emulsion stability parameter, S is that it is an indicator of the ability of an oil to form stable water-in-oil emulsions. S can have values in the range of 0 to 30. For a given oil, a value for S between 0 to 3 corresponds to a low ability for that oil to form water-in-oil emulsions. Even if such oils form water-in-oil emulsions, the emulsions will be unstable and will

easily demulsify upon coalescence and phase separation. Examples of such coalescence and phase separation means are centrifugal or electrostatic fields and percolation or passage through a porous sand bed. S values above about 3, indicate increasing ability for the oil to form stable water-in-oil emulsions.

[0010]   Any method that lowers the emulsion stability parameter, S, of a given oil will reduce its ability to form stable emulsions while increasing it will increase its ability to form stable water-in-oil emulsions.

[0011]   Some non-limiting examples of treatments of hydrocarbon oils that can result in a reduction in the S value of the oil are:

blending low asphaltene and low naphthenic acid containing oils with the oil,

thermal or electrochemical treatments of the oil under conditions where the total acid content is reduced, for example, thermal or catalytic decarboxylation,

chemical treatment of the oil where the naphthenic acid is chemically altered to a non-acidic form, for example conversion of the acids to an esters or ketones,

any treatment of the oil that extracts asphaltenes from the oil for example solvent deasphalting,

any treatment that extracts naphthenic acid from the oil.

[0012]   Some non-limiting examples of treatments of hydrocarbon oils that can result in an increase in the S value of the oil are:
thermal, biological or photochemical oxidation of the oil,

thermal or catalytic treatments that increase the amount of asphaltenes

blending with high asphaltenes and naphthenic acid containing oils,

addition of high molecular weight naphthenic acids or asphaltenes.

[0013]   The weight percent asphaltenes of an oil can be measured by

asphaltene precipitation and gravimetric methods. Solvents like n-pentane,

n-butane, n-hexane, n-heptane, cyclohexane and mixtures thereof can be

employed to precipitate asphaltenes from a hydrocarbon oil. The preferred

solvent for asphaltene precipitation is n-heptane. For example, to a weighed

amount of oil is added seven times its weight of n-heptane and the mixture

stirred for 10 hours at room temperature. The mixture is filtered through a 10

micron filter, the residue dried and weighed. The weight % n-heptane insoluble

asphaltenes is calculated from a knowledge of the initial weight of the oil and the

weight of the insoluble residue.

[0014]   The total acid number (TAN) of oil can be determined by potassium

hydroxide titration using the ASTM D-664 method. The weight in milligrams of

KOH required to neutralize 1 g of oil is the TAN of the oil. Other methods like

Fourier Transform Infra Red (FTIR) spectroscopy or liquid chromatography can

also be used. The TAN of the oil is a measure of the acid content of the oil.

[0015]   The molecular weight distribution of naphthenic acids can be

determined by chromatographic techniques, for example, high performance

liquid chromatography (HPLC). Analytical methods to determine the acidity of

oils and molecular weight distribution of acids are well known in the art. For

example, such procedures are disclosed in U.S. Patent 589776, which is

incorporated herein by reference. R, the ratio of 450+ molecular weight acids to

450 molecular weight acids can be calculated from the experimentally determined molecular weight distribution data.

[0016]   The oil comprising the water-in-oil emulsion can be any oil including crude oils, crude oil distillates, and hydrocarbon oil residue obtained from crude oil distillation or mixtures thereof. Through a determination of the emulsion stability parameter a method to prepare an unstable water-in-oil emulsion for a given oil is possible. The method comprises

measuring for the oil the weight percent asphaltenes, (A)

total acid number, (TAN)

ratio of the amount of naphthenic acids in the 450+ molecular weight to 450 molecular weight range (R),

calculating an emulsion stability parameter, S = A+ TAN * R
determining whether the emulsion stability parameter, S is greater than about 3, and, if above 3,

treating the oil to obtain a treated oil whose emulsion stability parameter S is less than about 3,

adding water in the range of 1 to 70 weight percent based on the weight of the treated oil to the said treated oil, and

mixing to form an unstable water-in-oil emulsion.

[0017]   The water content of the water-in-oil emulsions can vary in the range of 1 to 70 wt% based on the weight of the oil. The water comprising the water-in-oil emulsion can include halides, sulfate and carbonate salts of Group I and Group II elements of The Periodic Table of Elements, and mixtures thereof in a range of 0.01 wt% to 20 wt% based on the weight of water. The water-in-oil emulsion can have dispersed water droplets in the size range of 0.1 to 200 micron diameter.

[0018]   One process where preparing an unstable water-in-oil emulsion is important is in the process of desalting oils, particularly crude oils. An improved oil desalting method comprises measuring for the oil, the weight % asphaltenes (A),

total acid number (TAN),

ratio of the amount of naphthenic acids in the 450+ molecular weight to 450- molecular weight range (R);

calculating an emulsion stability parameter, $S = A + TAN * R$,

determining whether the emulsion stability parameter, S, is greater than about 3, and, if above 3;

treating the oil under conditions sufficient to obtain a treated oil whose emulsion stability parameter S is less than about 3;

adding water to the said treated oil, in the range of 1 to 20 wt% based on the weight of the treated oil;

mixing the treated oil and water to form a water-in-treated oil emulsion;

coalescing the water of the water-in- treated oil emulsion;

separating the coalesced water to obtain a desalted crude oil.

[0019]   The water droplets of the water-in-oil emulsion can be coalesced by methods such as but not limited to centrifugation, electrostatic treatment, hydrocyclone treatment, gravity settling and porous sand bed percolation.

[0020]   The following examples are non-limiting illustrations of the invention.

Calculation of emulsion stability parameter

[0021]   Seven crude oils, Talco, Tulare, Miandoum, Kome, Hamaca, Hoosier and Celtic were chosen. For each oil the following were measured:

Weight % n-heptane insoluble asphaltenes by precipitation and gravimetry
Total acid number (TAN) by KOH titration

The ratio of 450+ molecular weight to 450- molecular weight naphthenic acids by HPLC.

[0022]   The emulsion stability parameter S was calculated for each crude oil.

Experimental determination of emulsion stability: Procedure 1 (Berea Filtration or Porous Sand Bed Percolation)

[0023]   With each crude oil, the corresponding water-in-crude oil emulsion #1 was made at a ratio of 60% water:40% crude oil. To 40 g of the crude oil were

added 60 g of the corresponding synthetic brine and mixed. A Silverson mixer supplied by Silverson Machines, Inc. East Longmeadow, Massachusetts was used for mixing. Mixing was conducted at 25°C and at 400 to 600 rpm for a time required to disperse all the water into the oil. Water was added to the crude oil in aliquots spread over 5 additions.

[0024]   The stability of the emulsions was determined by passing the emulsions through a Berea sandstone column using procedure is described herein. A commercially available special fritted micro-centrifuge tube that is comprised of two parts is used as the container for the experiment. The bottom part is a tube that retains any fluid flowing from the top tube. The top part is similar to the usual polypropylene microcentrifuge tube, except that the bottom is a frit that is small enough to hold sand grains back, but allows the easy flow of fluid. In addition, the tubes come supplied with lids to each part, one of which serves also as a support that allows the top to be easily weighed and manipulated while upright. These micro-centrifuge tubes are available from Princeton Separations, Inc., Adelphia, New Jersey, and are sold under the name "CENTRI-SEP COLUMNS."

[0025]   A heated centrifuge is used to supply the pressure to flow the pusher fluid through a sand pack placed in the upper tube. The centrifuge supplied by Robinson, Inc., (Tulsa, OK) Model 620 was used. The temperature is set at 72°C. The top speed is about 2400 revolutions per minute (RPM) and the radius to the sandpack is 8 centimeters (cm), which gives a centrifugal force of 520 g. All weights are measured to the nearest milligram.

[0026]   The columns come supplied with a small supply of silica gel already weighed into the tube. This is discarded, and the weights of both sections noted. About 0.2 grams (g) of sand is weighed into the top and 0.2 ± 0.01 g of emulsion

added to the sandpack. Typical sands used for this experiment are Berea or Ottowa sands. For simplicity, one may use unsieved, untreated Ottawa sand. Alternatively, one may use one fraction that passes through 100 Tyler mesh, but is retained by a 150 mesh, and another fraction that passes through the 150 Tyler mesh, blended in a ten to one ratio respectively. The tube is weighed again, then centrifuged for one minute at full speed on the heated centrifuge. The bottom tube is discarded and the top is weighed again, which gives the amount of sand and emulsion remaining in the top. The sand is now in an emulsion wetted state, with air and emulsion in the pore spaces.

[0027] A bottom tube is weighed and placed below the top tube to capture the effluent during centrifugation. Both tubes are then centrifuged for a noted time (5 to 15 minutes). After centrifugation, the bottom tube was weighed again. The difference in weights is the weight of emulsion that passed through the sand-pack. The fluid in the bottom receptacle was drawn through a graduated micropipette. The amount of free water that had separated, if any, was noted. From knowledge of the amount of emulsion used in the experiment and the % water separated, emulsion stability was calculated as the wt% water retained by the emulsion.

Experimental determination of emulsion stability: Procedure 2 (Electrostatic Field)

[0028] With each crude oil, the corresponding water-in-crude oil emulsion #2 was made at a ratio of 20% water: 80% crude oil. To 80 g of the crude oil were added 20 g of the corresponding synthetic brine and mixed. A Silverson mixer supplied by Silverson Machines, Inc. East Longmeadow, Massachusetts was used for mixing. Mixing was conducted at 25°C and at 400 to 600 rpm for a time required to disperse all the water into the oil. Water was added to the crude oil in aliquots spread over 5 additions.

[0029]   The stability of prepared emulsions were determined by the electro-static demulsification technique. Electrostatic demulsification was conducted using a model EDPT-128™ electrostatic dehydrator and precipitation tester available from INTER-AV, Inc., San Antonio, Texas. Demulsification was conducted at an 830 volt/inch potential for 30 to 180 minutes at temperatures of 60 and 85°C. The amount of water separating from the electrostatic demulsifier tube was measured. From knowledge of the amount of emulsion used in the experiment and the % water separated, emulsion stability was calculated as the wt% water retained by the emulsion.

Correlation between experimentally determined emulsion stability and values calculated from the emulsion stability expression

[0030]   A plot of experimentally determined emulsion stability (Procedure 1) versus S is shown in Figure 1. A linear correlation is observed indicating the stability increases with increasing value of the emulsion stability parameter S.

[0031]   A plot of emulsion stability determined by Procedure 1 versus Procedure 2 is shown in Figure 2.

Method to prepare low stability water-in-oil emulsions aided by the emulsion stability expression

[0032]   Mixing 50 wt% Talco crude oil with 50 wt% isopar-M solvent, an oil mixture was made whose S had a value of 9.1. Using the correlation in Figure 1, the emulsion stability of the mixture is predicted to be about 48%. The experimentally determined value for the mixture based on Procedure 1 described above was 51% and based on Procedure 2 was 16%.

[0033]   Thus the method of blending two oils to lower the value of the emulsion stability parameter results in lowering the emulsion stability. The

method of blending two oils to lower the emulsion stability parameter is only an illustrative example and is not limiting. Any method that reduces the emulsion stability parameter can be employed.

CLAIMS:

1.   A method for determination for a given oil, the relative
stability of a water-in-oil emulsion that will be formed by that oil with water
comprising:

a)   measuring for the given oil the

(i)   weight percent asphaltenes (A),

(ii)   total acid number (TAN), and

(iii)   the ratio of the amount of naphthenic acids in the 450+ molecular
         weight to 450 molecular weight range (R);

b)   calculating an emulsion stability parameter, $S = A + TAN * R$;

c)   determining whether the emulsion stability parameter, S, is greater than
      about 3; with a value above 3 being determinative of an emulsion more
      stable than one with a value less than 3.

2.   The method of claim 1 wherein said oil is a crude oil, crude oil
distillate, resid from crude oil distillation and mixtures thereof.

3.   The method of claim 1 wherein said water comprises halides,
sulfate and carbonate salts of Group I and Group II elements of the Periodic
Table of Elements and mixtures thereof.

4.   The method of claim 1 wherein said water-in-oil emulsion has
dispersed water droplets in the size range of 0.1 to 200 micron diameter.

5.   A method to desalt an oil comprising:

a)   measuring for the oil, the

(i)   weight % asphaltenes (A),

(ii)   total acid number (TAN),

(iii)   the ratio of the amount of naphthenic acids in the 450+ molecular weight to 450 molecular weight range (R);

b)   calculating an emulsion stability parameter, $S = A + TAN * R$,

c)   determining whether the emulsion stability parameter, S, is greater than about 3, and, if above 3;

d)   treating the oil under conditions sufficient to obtain a treated oil whose emulsion stability parameter, S, is less than about 3;

e)   adding water to the said treated oil, in the range of 1 to 20 wt% based on the weight of the treated oil;

f)   mixing the treated oil and water to form a water-in-treated oil emulsion;

g)   coalescing the water of the water-in- treated oil emulsion;

h)   separating the coalesced water to obtain a desalted crude oil.

        6.   The method of claim 5 wherein said oil is a crude oil, crude oil distillate, resid from crude oil distillation and mixtures thereof.

        7.   The method of claim 5 wherein said treatment of the oil is selected form the group consisting of solvent deasphalting, thermal treatment for naphthenic acid reduction, electrochemical treatment for naphthenic acid reduction, blending with an oil having a S value less than 3, chemical treatment for naphthenic acid conversion to naphthenate ester, naphthenic acid extraction treatment and combinations thereof.

8.   The method of claim 5 wherein said coalescence is achieved by centrifugation, hydrocyclone treatment, electrostatic treatment, porous bed percolation and combinations thereof.

9.   A method to form an unstable water-in-oil emulsion from an oil and water comprising:

a)   measuring for the oil, the
   (i)   weight % asphaltenes (A),
   (ii)   total acid number (TAN),
   (iii)   the ratio of the amount of naphthenic acids in the 450+ molecular weight to 450- molecular weight range (R);

b)   calculating an emulsion stability parameter, $S = A + TAN * R$,

c)   determining whether the emulsion stability parameter, S, is greater than about 3, and, if above 3;

d)   treating the oil under conditions sufficient to obtain a treated oil whose emulsion stability parameter S is less than about 3;

e)   adding said water to the said treated oil, in the range of 1 to 20 wt% based on the weight of the treated oil;

f)   mixing the treated oil and the water to form an unstable water-in-treated oil emulsion.
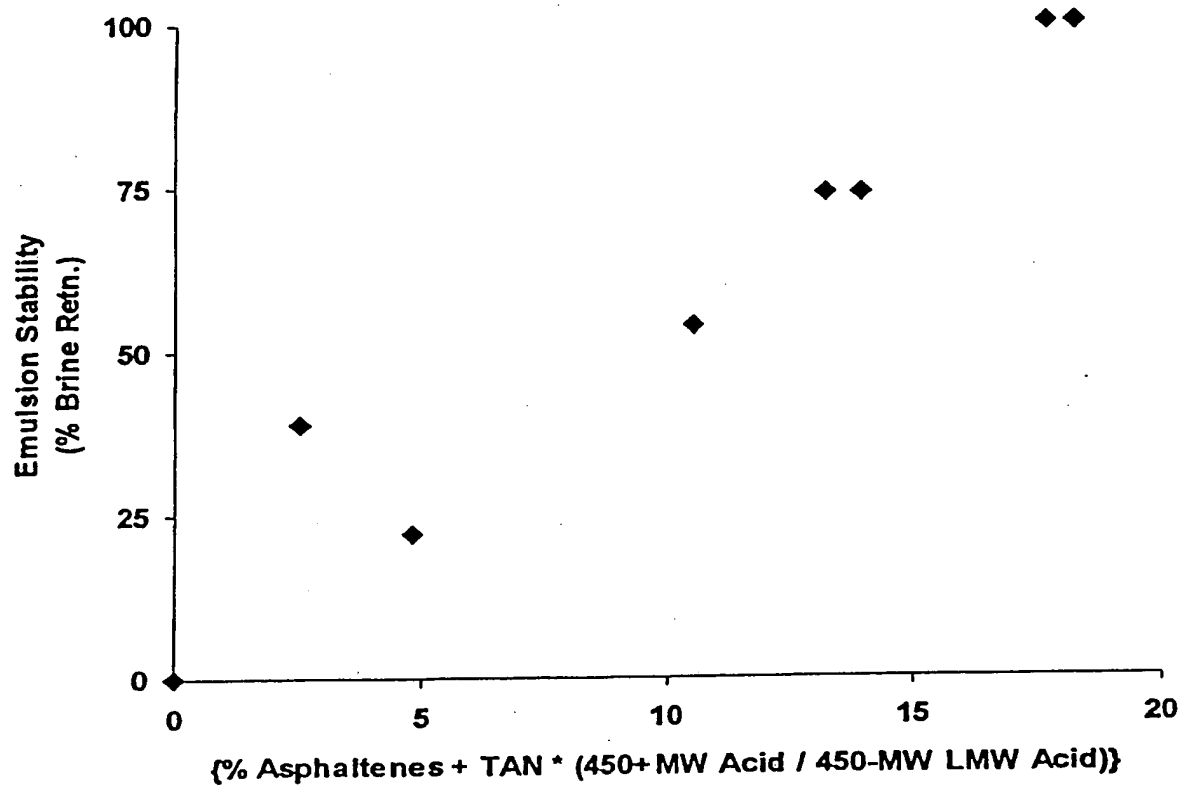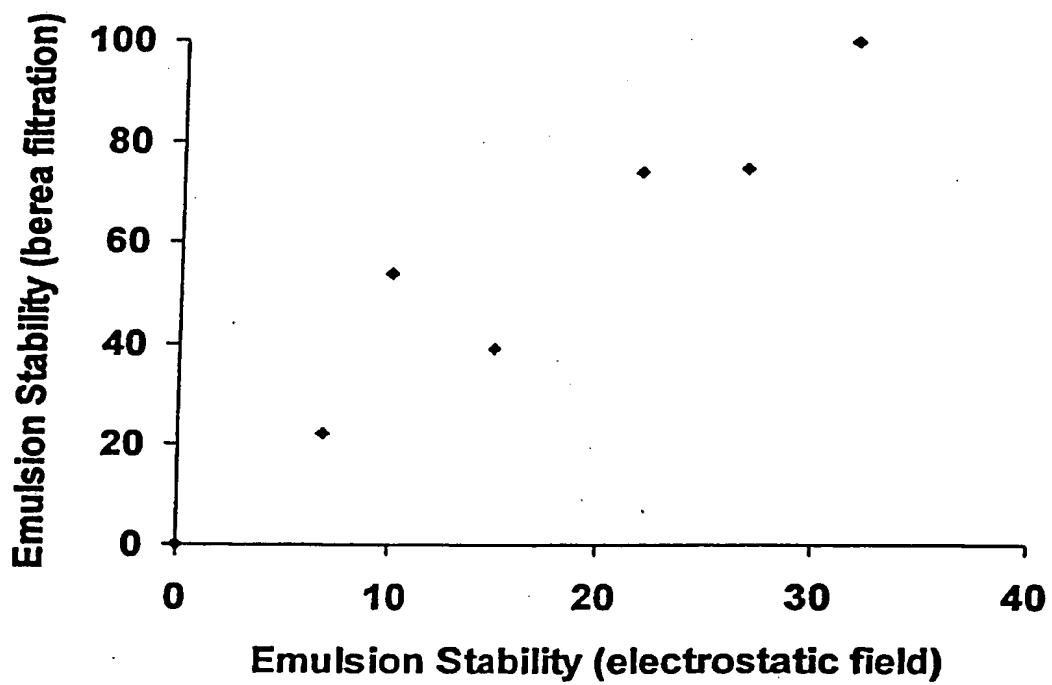
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FIG. 1

FIG. 2

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CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,
SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC,
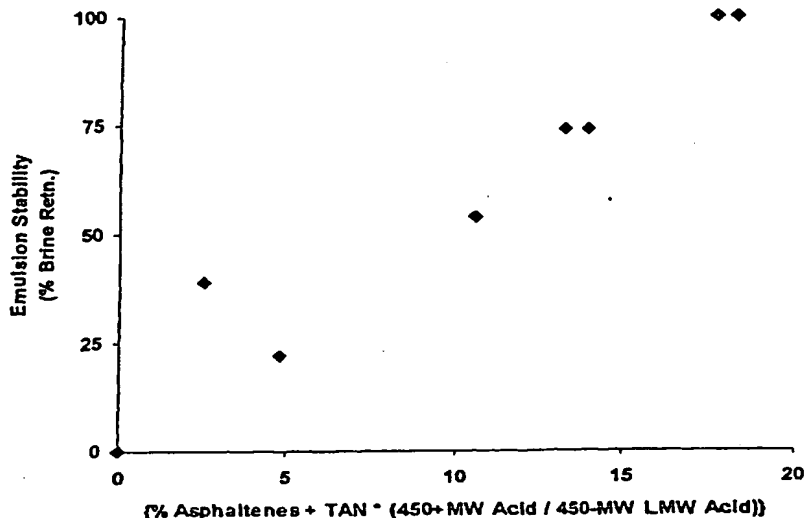VN, YU, ZA, ZM, ZW.

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European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
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(57) Abstract: A method for determination for a given oil the relative stability of a water-in-oil emulsion that will be formed by
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3 being determinative of an emulsion more stable than one with a value less than 3.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   C10G53/02   C10G31/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	STARK J L ET AL: "NEW METHOD PREVENTS DESALTER UPSETS FROM BLENDING INCOMPATIBLE CRUDES" OIL AND GAS JOURNAL, PENNWELL PUBLISHING CO. TULSA, US, vol. 100, no. 11, 18 March 2002 (2002-03-18), pages 89-91, XP001101619 ISSN: 0030-1388	5-7,9
A	page 90 -page 91; tables 3,4	1-4

X	US 2 904 485 A (LONG ROBERT B ET AL) 15 September 1959 (1959-09-15) column 1, line 15 -column 2, line 52; claim 1	5,6,9

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
8 October 2003	15/10/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Deurinck, P

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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